A Comprehensive Approach of Thermal Characterization of Batteries using Calorimetry

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Presented by:

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  - *Ph.D. (1990) Process Chemistry, Indian Institute of Technology, Delhi, India*
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  - *B.Sc. (1980) Chemistry, Zoology, Botany, Lucknow University, India*

- *Experience:*
  - *Dr. Singh is the Founder and President of Belmont Scientific, Inc. (BSI)*
  - *Prior to BSI, Dr. Singh held positions at:*
    - *Arthur D. Little, Inc.*
    - *TIAX, LLC*
    - *Exponent, Inc.*
    - *ioMosaic, Inc.*
    - *ioKinetic, LLC*

Introduction

- *Belmont Scientific, Inc. (BSI) is a contract research and testing laboratory located in Lowell, MA*

- *BSI provides testing and engineering solutions in the areas of:*
  - *Battery Design and Testing*
    - *Design Validation*
    - *Cycle life and calendar life testing*
    - *Thermal runaway characterization*
    - *Cell and battery pack vent design*
    - *Failure analysis*
  - *Process hazard analysis*
  - *Chemical reactivity*
  - *Pressure relief system design*

Characteristic Safety Parameters of Battery

- Onset temperature
- Cell heating rate
- Pressure rise rate
- Peak temperature
- Adiabatic temperature rise
- Total heat generation (heat of reaction)
- Amount of gas generation
- Voltage drop temperature
- Vent opening temperature
- Vent opening pressure
- Fraction of heat from cell casing vs. vent (ejecta heat)

Calorimetric Techniques

- **DSC** (Differential Scanning Calorimeter) :
  - Sample size: 2-20mg
  - Test material: raw material and charged battery components
  - Onset T, ***Peak T, Heat of reaction***

- **ARC** (Accelerating Rate Calorimeter):
  - Sample size: 0.5g to 5g
  - Battery type: Lithium-ion
  - Test Articles:
    - Cylindrical cells (18650 to 21700)
    - Pouch cells (small)
    - ***Onset T, dT/dt, dP/dt, Peak T***, total heat release
    - EV+ ARC can accommodate larger cell

- **TRC** (Thermal runaway calorimeter):
  - Sample: Any cell size and shape
  - Onset T, peak T, total heat release
  - Battery type: Lithium-ion, **Lithium metal**
  - Onset T, ***dT/dt, Peak T,*** **total heat release, amount of gas generated,** Peak P

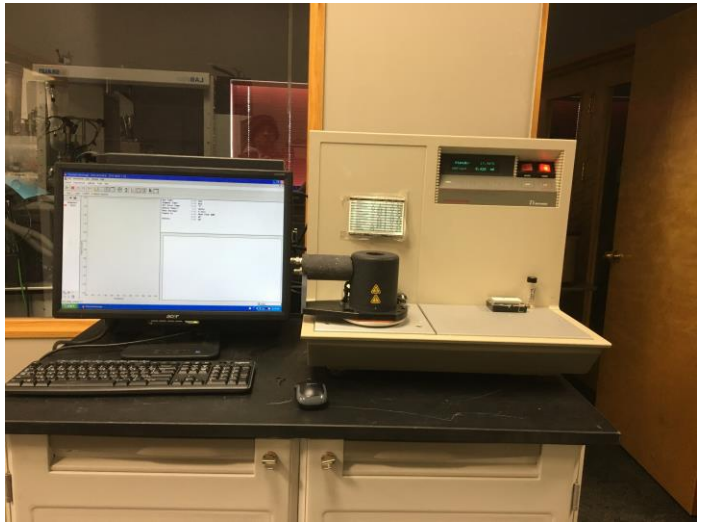
- **FTRC** (Fractional thermal runaway calorimeter):
  - Sample: Moderate size and any shape
  - Test Articles: **Li-ion, Li-metal**
    - Cylindrical cells (18650 , 21700)
    - Pouch/prismatic cells
    - **total heat release, fraction of heat release from cell casing vs. vent as ejecta heat**

Approach

- DSC
- ARC
- TRC
- FTRC

DSC Testing of Battery Materials

- Sample
  - 2-20mg battery materials
  - Raw material or material from charged cell
- Test cell
  - SS-316, high pressure test cell (110bar)
  - Volume of cell: 30 micro liter
  - Weight of cell : 700 mg

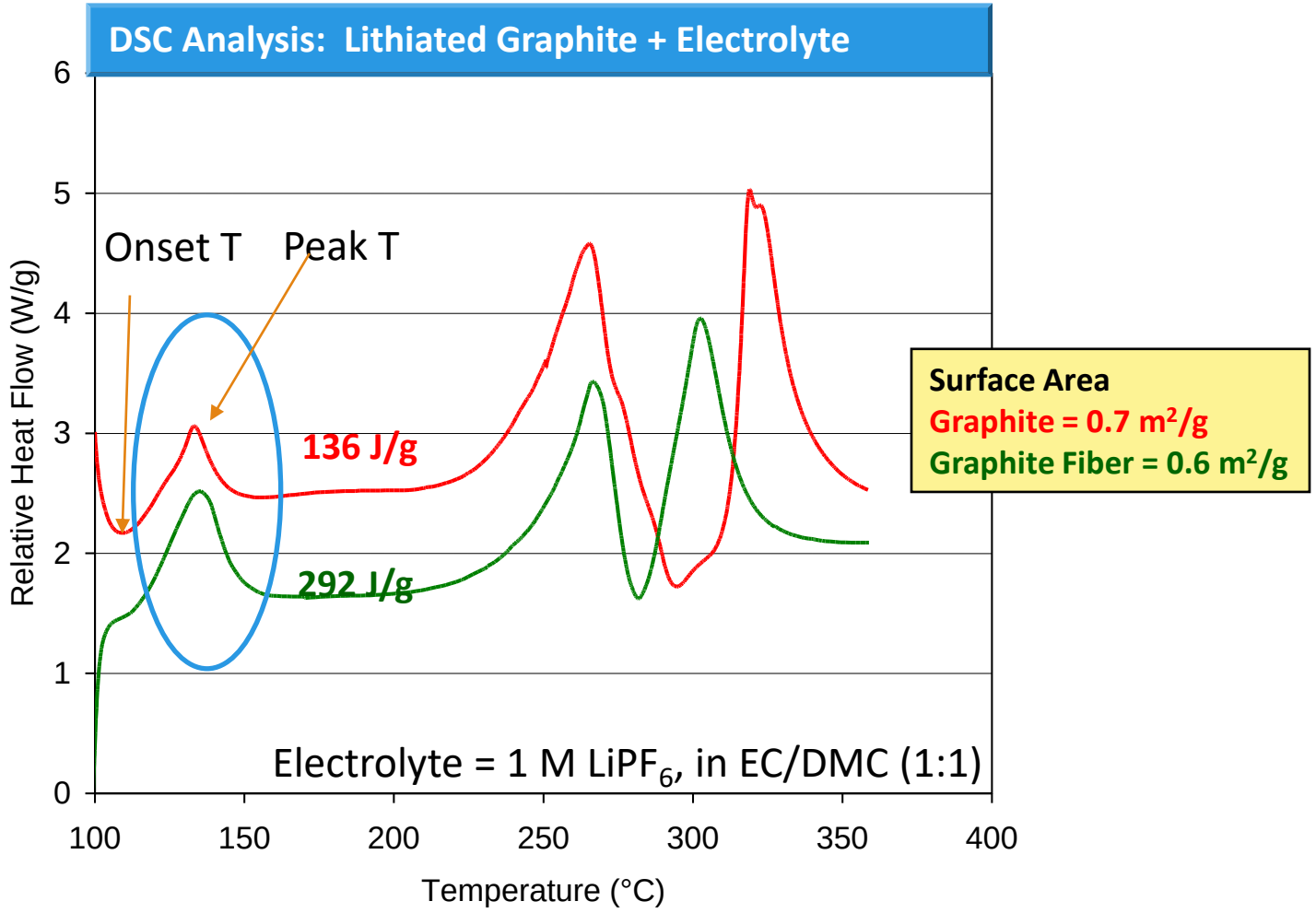


Differential scanning calorimeter (DSC)

High pressure test cell

DSC Testing of Lithiated Graphite

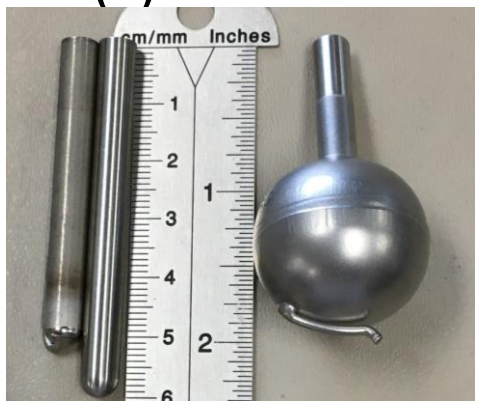
- Sample
  - 20mg Lithiated graphite
    - Graphite = 0.7 m^2/g
    - Graphitic fiber = 0.6 m^2/g
  - 20 mg 1M LiPF6, in EC/DMC (1:1)
- Significant difference in heat of reaction although number of peaks and onset temperature is same

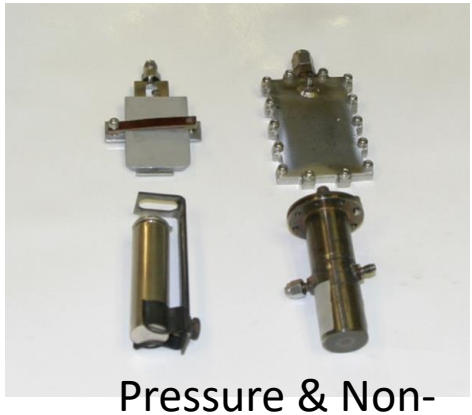


ARC measurements

- Information about complete cell can be investigated and inherently safe batteries can be designed by careful material selection
- ARC calorimeter provides critical and accurate information on key chemical matrix
  - Onset temperature of exothermic reaction (S)
  - Self heating rate
  - Pressure
  - Pressure generation rate
  - Heat of reaction

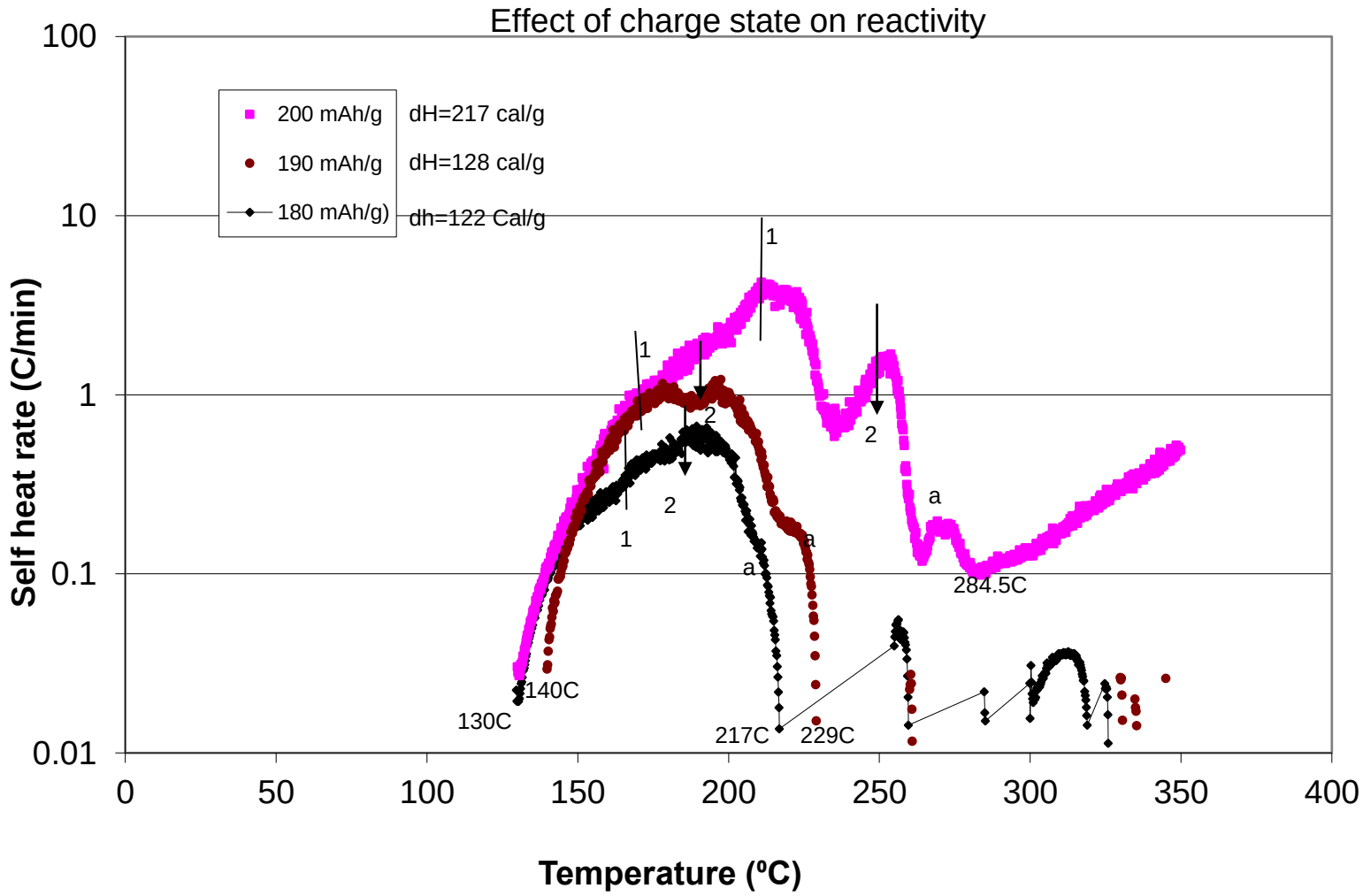
Netzsch ARC 254





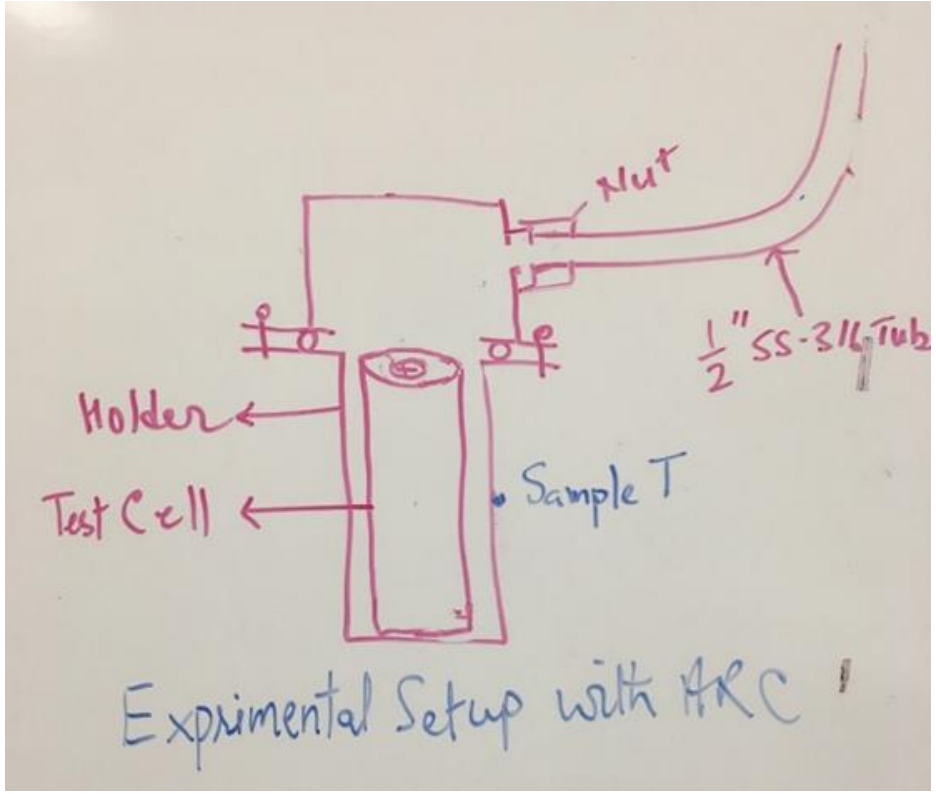
Pressure & Non-pressure ARC holders

ARC results show effect of charge state on reactivity of NCA cathode material

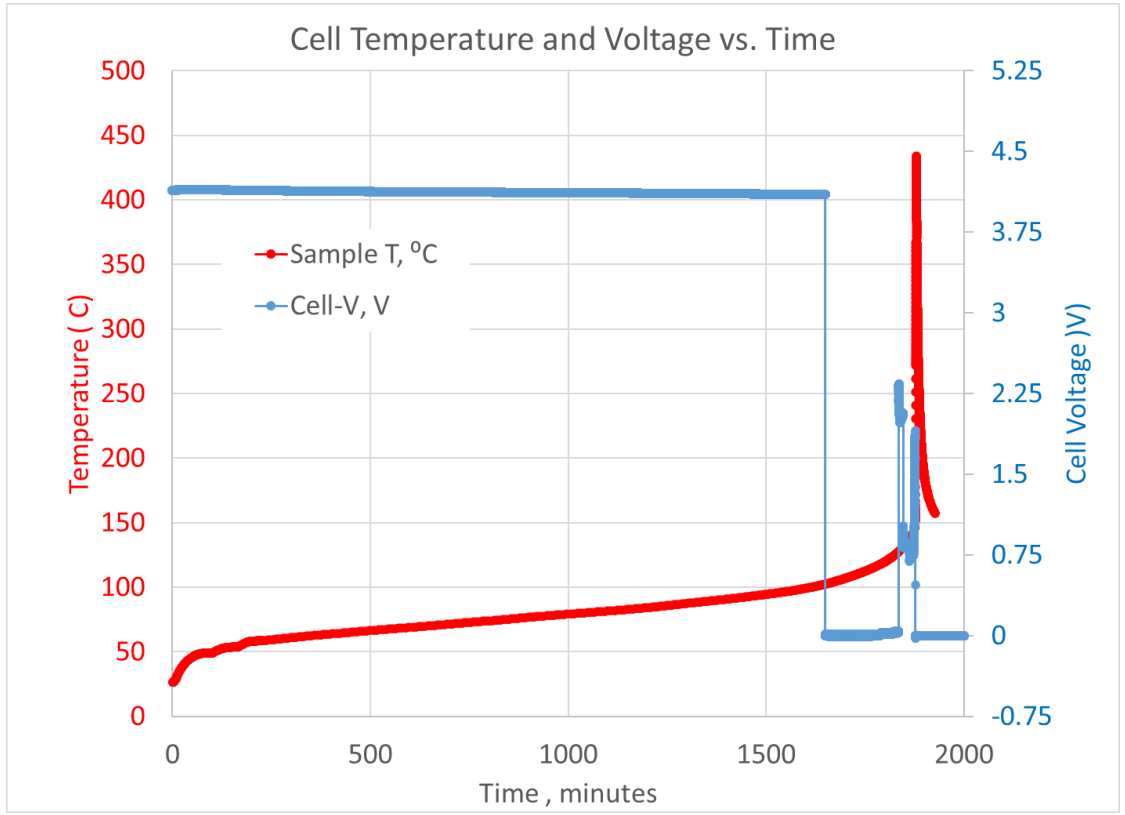


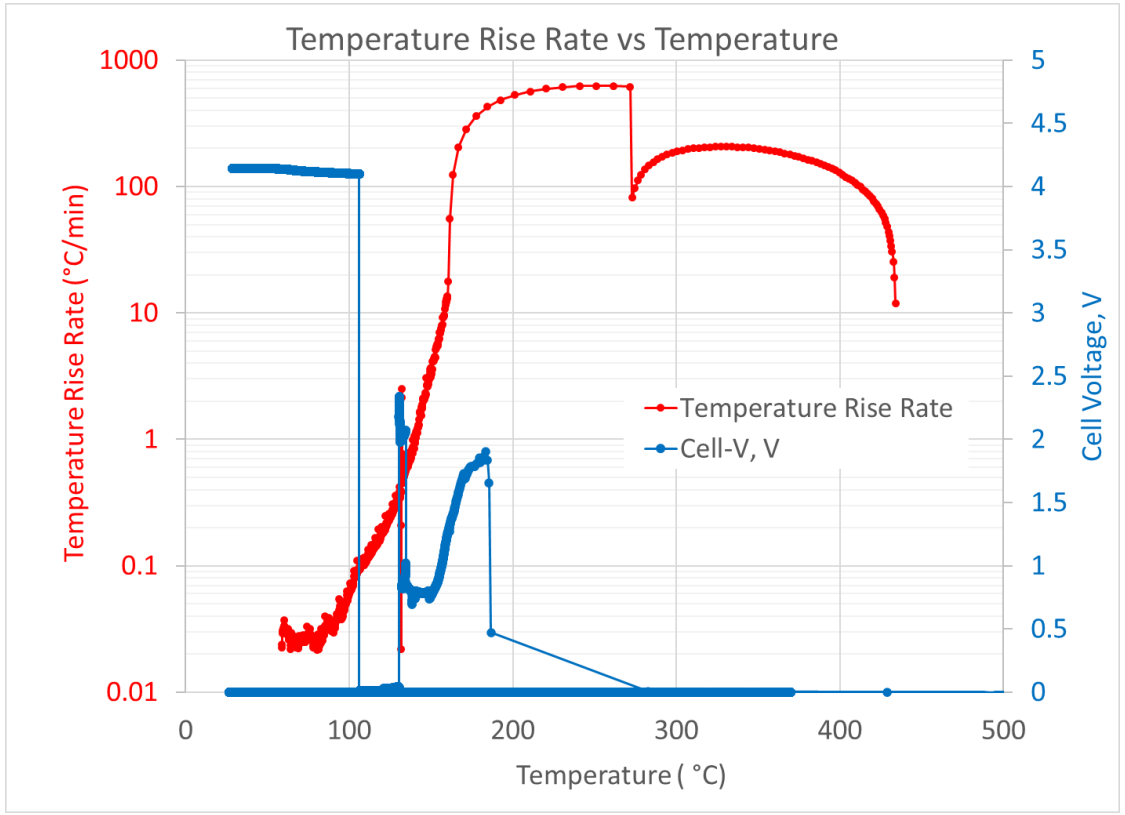
Description of ARC® Experiments

- A cylindrical 21700 at 100% SOC was placed inside the ARC holder. Then ARC holder was places inside the calorimeter
- Cell voltage and temperature was recorded throughout the test along with multiple thermocouples on holder and tube to record the change in temperature.
- Test Parameter:
  - Heat-Wait-Search heating mode
  - Temperature range: 50-400°C
  - Exotherm detection limit: 0.02°C/min
  - Thermal inertia: 2.94
  - Max. adiabatic tracking : 15°C/min



Description of ARC Experiments

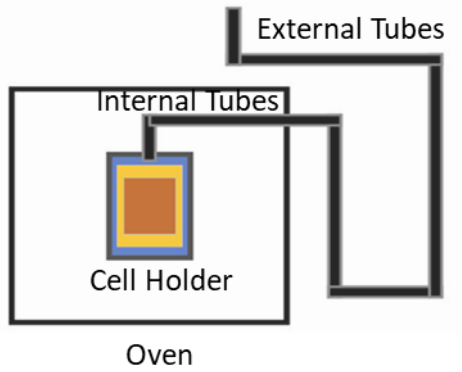




Cell ID	Results	Wt. Loss	Onset T at 0.03 ˚C/min	T at Max SHR	Max SHR	End T	Adiabatic T Rise	Heat of Reaction	T at Drop in SHR	Voltage Drop T
Typical		%	˚C	˚C	˚C/min	˚C	˚C	kJ	˚C	˚C
21700,	Exotherm	66	85	130.7	0.42	131.5	138	10.12	132	109
100%	Exotherm		132	251.2	627	434.0	890	65.47		

Description of TRC Experiments

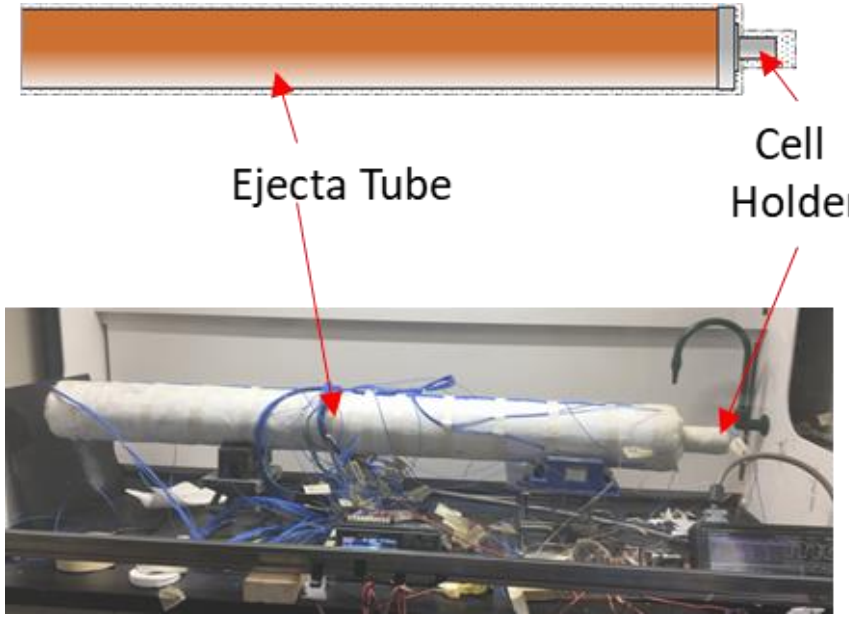
- A cylindrical 21700 at 100% SOC was placed inside the TRC holder. Then TRC holder was places inside the oven and connected with insulated pipe
- Holder was heated by *heating oven at 2 °C/min from room temperature to 200°C*
  - Cell voltage and temperature was recorded throughout the test along with dozens of thermocouples on holder and different sections of pipe to record the change in temperature.
  - Total heat of reaction measured was



Cell ID	Initial Voltage	Weight Loss	Max. Cell T	Oven Heating Rate	Total Energy Release
Typical	V	%	˚C	˚C/min	kJ
21700	4.15	66	1096	1.88	99

Description of FTRC Experiments

- A cylindrical 21700 at 100% SOC was placed inside the FTRC holder. Then FTRC holder was connected to ejecta tube
- Cell was *heated at 2 °C/min from room temperature to 200°C using flexible heater over cell*
  - Cell voltage and temperature was recorded throughout the test along with dozens of thermocouples on holder and ejecta tube to record the change in temperature.
  - Total heat of reaction measured was



Test #	Cell Type*	Initial Voltage, V	Weight Loss Percent, %	Maximum Cell T, ˚C	Cell Vent Open T, ˚C	Total Energy, kJ	Cell Can Energy, kJ	Ejecta Energy, kJ	Cell Can Fraction	Cell Ejecta Fraction
1	21700	4.177	86.46	218.6	155	121	4	117	0.03	0.97
2	21700	4.225	86.42	218.6	155	122	6	116	0.05	0.95
3	21700	4.147	86.88	268.6	155	126	8	118	0.06	0.94
4	21700	4.137	86	343	155	115	11	104	0.13	0.87
5	21700	4.171	63.93	572.2	155	111	25	86	0.23	0.77
AVG		***4.17***	***82***	***324***	***155***	***119***	***11***	***108***	***0.10***	***0.90***
AVE DEV		***0.02368***	***7.2032***	***106.72***	***0***	***4.8***	***5.76***	***10.56***	***0.064***	***0.064***

*Cylindrical cell 21700, 100%SOC

Summary of ARC, TRC and FTRC

Parameters	DSC	ARC	TRC	FTRC
Onset Temperature	X	X	X	
Cell heating rate		X	X	
Pressure rise rate		X	X	
Peak temperature / pressure	X	X	X	
Adiabatic temperature rise		X		
Amount of heat generation	X	X	X	X
Amount of gas generation		X	X	X
Vent opening temperature		X	X	X
Vent opening pressure		X	X	X
Fraction of heat from cell casing vs. Ejecta heat			X	X
Voltage drop Temperature or Separator shutdown temperature		X	X	X

X : Best
X : OK
X : Poor

Conclusion

- DSC and ARC both can be used for thermal characterization of battery including onset T, peak reaction T and heat of reaction of battery materials but DSC provides the most accurate heat of reaction (total energy release).
- ARC is an excellent tool to measure accurate onset T, cell heating rate, adiabatic temperature rise and heat of reaction if peak cell heating rate is below adiabatic tracking rate (15 C/min for standard ARC).
- TRC is a better technique than ARC for determination of cell heating rates, pressure rise rate, peak temperature, and total amount of heat release where cell heating rates are above 15C/min. TRC is design to test any size, shape and chemistry of the cell
- FTRC is a technique to determine total energy release in the event of thermal runaway. It also provides the fraction of energy release through cell casing vs ejecta energy

Thank You

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